

PATENT COOPERATION TREATY

PCT

From the INTERNATIONAL BUREAU

**NOTIFICATION CONCERNING
THE FILING OF AMENDMENTS OF THE CLAIMS**
(PCT Administrative Instructions, Section 417)

To:

BRANTS, Johan, Philippe, Emile
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Belgium

Date of mailing (day/month/year) 27 January 2004 (27.01.2004)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference TES-011-PCT	
International application No. PCT/EP2003/005799	International filing date (day/month/year) 03 June 2003 (03.06.2003)
Applicant TESSENDERLO CHEMIE S.A. et al	

1. The applicant is hereby notified that amendments to the claims under Article 19 were received by the International Bureau on:

21 January 2004 (21.01.2004)

2. This date is within the time limit under Rule 48.1.

Consequently, the international publication of the international application will contain the amended claims according to Rule 48.2(f), (h) and (i).

3. The applicant is reminded that the international application (description, claims and drawings) may be amended during the international preliminary examination under Chapter II, according to Article 34, and in any case, before each of the designated Offices, according to Article 28 and Rule 52, or before each of the elected Offices, according to Article 41 and Rule 78.

<p>The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland</p> <p>Facsimile No. (41-22) 338-7080</p>	<p>Authorised officer</p> <p>Bruno LE FEUVRE</p> <p>Telephone No. (41-22) 338 7096</p>
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Confirmation by special mail

Sint-Martens-Latem, January 21, 2004

Our ref. : TES-011-PCT
Re. : PCT Application N° PCT/EP03/05799 filed on June 3, 2003
In the name of Tessenderlo Chemie N.V.

Dear Sirs,

Further to your Notification of Transmittal of the ISR (PCT rule 44.1), an amended set of claims is herewith submitted according to Art. 19 PCT with respect to the above mentioned patent application.

Claims 1, 15 and 19 are replaced by amended claims bearing the same numbers; claims 2-14, 16-18 and 20-29 are unchanged. For sake of clarity a marked up version of the claims are also enclosed herein.

Respectfully submitted,



BRANTS, Johan Philippe Emile
Professional Representative before the EPO

Enclosures : Confirmation sheet (please return)
Replacement sheets (clean version amended set of claims) (3x)
Marked up version of the amended claims (3x)

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Claims

1. A method for the preparation of halogenated benzonitriles by vapour phase ammoxidation of halogenated C_1 to C_6 alkyl benzenes, in the presence of water vapour, at a reaction temperature comprised in the range of 300 to 500 °C, using a three-component catalyst into a fixed bed reactor wherein said catalyst consists of a promoted VPO active phase provided on a carrier.
2. A method according to claim 1, wherein said reaction temperature is comprised in the range of 350 to 450 °C.
3. A method according to claim 1 or 2, wherein the residence time of the halogenated C_1 to C_6 alkyl benzene in said reactor is less than 10 seconds, preferably less than 8 seconds.
4. A method according to any of claims 1 to 3, wherein said halogenated C_1 to C_6 alkyl benzene is di- or tri-halogenated C_1 to C_6 alkyl benzene.
5. A method according to claim 4, wherein said di- or tri-halogenated C_1 to C_6 alkyl benzene is di-halogenated toluene.
6. A method according to claim 5, wherein said di-halogenated toluene is 2,6-dichlorotoluene.
7. A method according to any of claims 1 to 6, wherein said catalyst is provided on an Al_2O_3 carrier.
8. A method according to any of claims 1 to 6, wherein said catalyst is provided on a TiO_2 carrier.
9. A method according to claim 8, wherein said TiO_2 carrier consists of the anatase phase.
10. A method according to any of claims 1 to 9, wherein said catalyst comprises a $V_1P_aM_bAl_cO_x$ or $V_1P_aM_bTi_cO_x$ catalyst wherein M is chosen from the group comprising Cr, Fe, Co and Mo; a is 0.1 - 2.0; b is 0.002 - 1.0; c is 2.0 - 10.0, and x is determined by the valences of other component elements.
11. A method according to claim 10, wherein M is Co or Cr.
12. A method according to any of claims 1 to 11, whereby the catalyst is diluted with an inert medium in the ratio of 0.5 to 2.0 by weight with respect to the weight of said catalyst prior to its addition to the reactor.

13. A method according to claim 12 wherein said inert medium comprises corundum particles, porcelain beads, quartz beads, glass beads or the like.
14. A method according to any of claims 1 to 13, comprising the step of supplying a halogenated alkane to said reactor.
- 5 15. A VPO catalyst, suitable for use in a method according to any of claims 1 to 14, obtainable by a process comprising the steps of
 - preparing a bulk VPO precursor;
 - impregnating said bulk VPO precursor with a promoter element in order to obtain a bulk promoted VPO precursor; and
 - 10 - adding a carrier to said bulk promoted VPO precursor,
 - and calcining the resultant mixture under a weakly oxidising atmosphere of O_2/N_2 to obtain a supported and promoted VPO catalyst,

whereby said catalyst is a $V_1P_aM_bAl_cO_x$ or $V_1P_aM_bTi_cO_x$ catalyst wherein M is chosen from the group comprising Cr, Fe, Co and Mo; a is 0.1 - 2.0; b is 0.002 - 1.0; c is 2.0 - 10.0, and x is determined by the valences of other component elements.
- 15 16. A catalyst according to claim 15, wherein said carrier is an Al_2O_3 carrier.
17. A catalyst according to claim 15, wherein said carrier is a TiO_2 carrier.
18. A catalyst according to claim 17, wherein said TiO_2 carrier consists of the anatase phase.
- 20 19. A method for the preparation of a catalyst according to any of claims 15 to 18 comprising the steps of:
 - preparing a bulk VPO precursor;
 - impregnating said bulk VPO precursor with a promoter element in order to obtain a bulk promoted VPO precursor; and
 - 25 - adding a carrier to said bulk promoted VPO precursor,
 - and calcining the resultant mixture under a weakly oxidising atmosphere of O_2/N_2 to obtain a supported and promoted VPO catalyst.
20. A method according to claim 19 comprising the steps of:
 - refluxing of a vanadium source in the presence of alcohols to obtain a solution containing reduced vanadium species;
 - 30

- adding of a phosphorus source and refluxing said solution in order to obtain a bulk VPO precursor;
 - impregnation of said bulk VPO precursor with an alcoholic or aqueous solution of a promoter element to obtain a bulk promoted VPO precursor;
 - 5 - mixing said bulk promoted VPO precursor with $\gamma\text{-Al}_2\text{O}_3$ or TiO_2 carrier powder; and shaping and calcining the resultant mixture to obtain a supported and promoted VPO catalyst.
21. A method according to claim 19 or 20, wherein said vanadium source is V_2O_5 and said phosphorous source is $\text{o-H}_3\text{PO}_4$.
- 10 22. A method according to any of claims 19 to 21, wherein said promoter element comprises Cr, Fe, Co or Mo.
23. A method according to any of claims 19 to 22, wherein the ratio of said bulk promoted VPO precursor over said $\gamma\text{-Al}_2\text{O}_3$ or TiO_2 carrier powder is comprised in the range of 1:2 to 1:10, preferably 1:6.
- 15 24. A method according to any of claims 19 to 23, wherein the calcining step is performed at a temperature comprised in the range of 300 to 900°C for a period of 1 to 10 hours, under a calcining atmosphere.
25. A method according to any of claims 19 to 23, wherein the calcining step is performed at a temperature comprised in the range of 350 to 700°C for a period of 2 to 6
- 20 hours, under a calcining atmosphere of weak oxidising strength.
26. Use of a VPO catalyst according to any of claims 15 to 18 and prepared according to any of claims 20 to 26 in a vapour phase ammoxidation reaction.
27. Use of a VPO catalyst according to claim 26 in a vapour phase ammoxidation reaction according to any of claims 1 to 15.
- 25 28. Use of a VPO catalyst according to claim 27 for preparing 2,6-dichlorobenzonitrile from 2,6-dichlorotoluene in a vapour phase ammoxidation reaction.
29. Use of a VPO catalyst according to claim 28 in a vapour phase ammoxidation reaction of hetero aromatic hydrocarbons.

Claims (marked up version)

1. A method for the preparation of halogenated benzonitriles by vapour phase ammoxidation of halogenated C₁ to C₆ alkyl benzenes, in the presence of water vapour,
5 at a reaction temperature comprised in the range of 300 to 500 °C, using a three-component catalyst into a fixed bed reactor wherein said catalyst consists of a promoted VPO active phase provided on a carrier.
2. A method according to claim 1, wherein said reaction temperature is comprised in the range of 350 to 450 °C.
- 10 3. A method according to claim 1 or 2, wherein the residence time of the halogenated C₁ to C₆ alkyl benzene in said reactor is less than 10 seconds, preferably less than 8 seconds.
4. A method according to any of claims 1 to 3, wherein said halogenated C₁ to C₆ alkyl benzene is di- or tri-halogenated C₁ to C₆ alkyl benzene.
- 15 5. A method according to claim 4, wherein said di- or tri-halogenated C₁ to C₆ alkyl benzene is di-halogenated toluene.
6. A method according to claim 5, wherein said di-halogenated toluene is 2,6-dichlorotoluene.
7. A method according to any of claims 1 to 6, wherein said catalyst is provided on
20 an Al₂O₃ carrier.
8. A method according to any of claims 1 to 6, wherein said catalyst is provided on a TiO₂ carrier.
9. A method according to claim 8, wherein said TiO₂ carrier consists of the anatase phase.
- 25 10. A method according to any of claims 1 to 9, wherein said catalyst comprises a V₁P_aM_bAl_cO_x or V₁P_aM_bTi_cO_x catalyst wherein M is chosen from the group comprising Cr, Fe, Co and Mo; a is 0.1 - 2.0; b is 0.002 - 1.0; c is 2.0 - 10.0, and x is determined by the valences of other component elements.
11. A method according to claim 10, wherein M is Co or Cr.
- 30 12. A method according to any of claims 1 to 11, whereby the catalyst is diluted with an inert medium in the ratio of 0.5 to 2.0 by weight with respect to the weight of said catalyst prior to its addition to the reactor.

13. A method according to claim 12 wherein said inert medium comprises corundum particles, porcelain beads, quartz beads, glass beads or the like.
14. A method according to any of claims 1 to 13, comprising the step of supplying a halogenated alkane to said reactor.
- 5 15. A VPO catalyst, suitable for use in a method according to any of claims 1 to 14, obtainable by a process comprising the steps of
 - preparing a bulk VPO precursor;
 - impregnating said bulk VPO precursor with a promoter element in order to obtain a bulk promoted VPO precursor; and
 - 10 - adding a carrier to said bulk promoted VPO precursor,
 - and calcining the resultant mixture under a weakly oxidising atmosphere of O₂/N₂ to obtain a supported and promoted VPO catalyst,

whereby said catalyst is a V₁P_aM_bAl_cO_x or V₁P_aM_bTi_cO_x catalyst wherein M is chosen from the group comprising Cr, Fe, Co and Mo; a is 0.1 - 2.0; b is 0.002 - 1.0; c is 2.0

- 15 - 10.0, and x is determined by the valences of other component elements.
- 16. A catalyst according to claim 15, wherein said carrier is an Al₂O₃ carrier.
- 17. A catalyst according to claim 15, wherein said carrier is a TiO₂ carrier.
- 18. A catalyst according to claim 17, wherein said TiO₂ carrier consists of the anatase phase.
- 20 19. A method for the preparation of a catalyst according to any of claims 15 to 18 comprising the steps of:
 - preparing a bulk VPO precursor;
 - impregnating said bulk VPO precursor with a promoter element in order to obtain a bulk promoted VPO precursor; and
 - 25 - adding a carrier to said bulk promoted VPO precursor, ~~in order to obtain a VPO catalyst;~~
 - and calcining the resultant mixture under a weakly oxidising atmosphere of O₂/N₂ to obtain a supported and promoted VPO catalyst.
- 20. A method according to claim 19 comprising the steps of:
 - 30 - refluxing of a vanadium source in the presence of alcohols to obtain a solution containing reduced vanadium species;

- adding of a phosphorus source and refluxing said solution in order to obtain a bulk VPO precursor;
 - impregnation of said bulk VPO precursor with an alcoholic or aqueous solution of a promoter element to obtain a bulk promoted VPO precursor;
- 5 - mixing said bulk promoted VPO precursor with $\gamma\text{-Al}_2\text{O}_3$ or TiO_2 carrier powder; and shaping and calcining the resultant mixture to obtain a supported and promoted VPO catalyst.
21. A method according to claim 19 or 20, wherein said vanadium source is V_2O_5 and said phosphorous source is $\text{o-H}_3\text{PO}_4$.
- 10 22. A method according to any of claims 19 to 21, wherein said promoter element comprises Cr, Fe, Co or Mo.
23. A method according to any of claims 19 to 22, wherein the ratio of said bulk promoted VPO precursor over said $\gamma\text{-Al}_2\text{O}_3$ or TiO_2 carrier powder is comprised in the range of 1:2 to 1:10, preferably 1:6.
- 15 24. A method according to any of claims 19 to 23, wherein the calcining step is performed at a temperature comprised in the range of 300 to 900°C for a period of 1 to 10 hours, under a calcining atmosphere.
25. A method according to any of claims 19 to 23, wherein the calcining step is performed at a temperature comprised in the range of 350 to 700°C for a period of 2 to 6
- 20 hours, under a calcining atmosphere of weak oxidising strength.
26. Use of a VPO catalyst according to any of claims 15 to 18 and prepared according to any of claims 20 to 26 in a vapour phase ammoxidation reaction.
27. Use of a VPO catalyst according to claim 26 in a vapour phase ammoxidation reaction according to any of claims 1 to 15.
- 25 28. Use of a VPO catalyst according to claim 27 for preparing 2,6-dichlorobenzonitrile from 2,6-dichlorotoluene in a vapour phase ammoxidation reaction.
29. Use of a VPO catalyst according to claim 28 in a vapour phase ammoxidation reaction of hetero aromatic hydrocarbons.